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Polyester Production Method

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SPECIFICATION

Detailed Explanation of the Invention

The present invention relates to a method for producing polyester from an aromatic dibasic acid and ethylene glycol. Its object is to prevent lowering of the melting point and lessen the drawbacks of the polyester polymers obtained. Secondary reactions such as etherification of the ethylene glycol occur when polyester is manufactured from an aromatic dibasic acid and ethylene glycol. As a result, it is well known that the softening point of the polyester obtained is lower than that of polyester manufactured by transesterification or from a bisglycol ester. Addition of various additives has been proposed to prevent this. The catalyst of the present invention is one of these. Alkali metals, alkaline earth metals, and compounds thereof are well known as conventional additives to prevent lowering of the softening point. However, it is generally desirable both to obtain catalytic action and to prevent lowering of the softening point. Ammonium halides, tertiary amines, and ammonium salts of weak acids are frequently recommended as compounds that have these effects. However, they color the product brown and cause an off-odor when used in esterification at high temperature under increased pressure. Consequently, they can only be used at low temperature under normal pressure. Therefore, reaction of a large amount of ethylene glycol by use of such compounds requires a long time and is known to be economically unfeasible from an industrial standpoint.

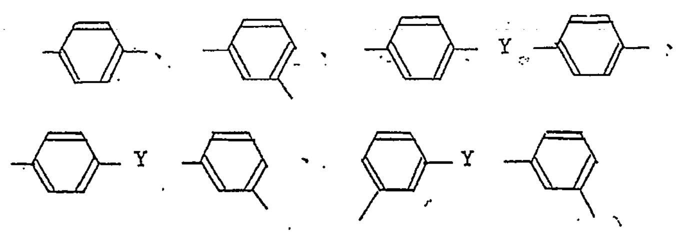
Ordinary compounds known and used as catalysts usually do little to prevent lowering of the softening point. Addition of separate agents to prevent lowering of the softening point, such as the aforementioned alkali and alkaline earth metals, consequently is necessary. The alkali and alkaline earth compounds added in this case cannot be expected to have satisfactory effects if an excess of metal is not added, because their effects are reduced by the formation of salt with the aromatic dibasic acid. The dibasic acid salts produced in this case also cause various problems in spinning and film formation steps, lead to the inclusion of foreign matter in fibers and films, and result in serious drawbacks to the product value of the fibers and films.

The present invention is characterized by using double salts obtained by reacting aluminic acid esters and compounds selected from among alkali metals, alkaline earth metals and halides, alkoxides, glycolates, and phenoxides thereof in ethylene glycol as the catalyst and additive. These double salts conspicuously prevent lowering of the softening point of the polymer produced and, at the same time, have excellent effects as catalyst when polyester is produced from an aromatic dibasic acid and ethylene glycol. The aforementioned salts accelerate the esterification of the dibasic acid and ethylene glycol at high temperature under reduced pressure well and satisfactorily prevent lowering of the softening point. Also, they do not precipitate as foreign matter, since they remain dissolved in the reaction system.

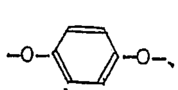
Aromatic dicarboxylic acids represented by the following general formula are used in implementation of the method of the present invention.

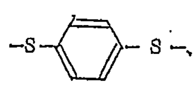
$$HOOCR_1XR_2\text{-}COOH$$

[R_1 and R_2 are -(CH_2)- (n is 0 or 1-4), X is a bivalent aromatic residue represented by



Y is a bivalent residue represented by -$(CH_2)_n$-, -$(CH_2)_n$-CO-$(CH_2)_n$-, -$(CH_2)_n$-O-$(CH_2)_n$-,

-O-$(CH_2)_m$-O-, 

-$(CH_2)_n$-S-$(CH_2)_n$-, -S-$(CH_2)_n$-S-, 

-SO_2-, or =N-$(CH_2)_n$-CH_3, n is 0 or 1-4, and m is 1-5.]

The double salts used in the present invention are double salts formed when an aluminic acid ester represented by the general formula $Al(OR)_3$ (wherein R is an alkyl group such as methyl, ethyl, propyl, or isopropyl, an allyl group such as phenyl or tolyl, a cycloalkyl group such as cyclohexyl, or an aralkyl group such as benzyl) and a compound selected from among alkali metals such as lithium, sodium, and potassium, alkaline earth metals such as magnesium, calcium, strontium, and barium, or hydrides, alkoxides, glycolates, or phenoxides thereof are dissolved by heating at 150-200°C in ethylene glycol and allowed to react for approximately 1 hour. They are hypothesized to have a structure shown by $M[Al(OCH_2CH_2OH)(OR)_3]n'$ (wherein M is the aforementioned metal ion, n′ is the valence of the aforementioned metal, and R is the same as R in the aforementioned aluminic acid esters). It is preferable to use 1 mol of alkali metal or compound thereof or 0.5 mol of alkaline earth metal or compound thereof per mole of aluminic acid ester when producing these double salts.

These double salts can be used as they are in the reaction of an aromatic dicarboxylic acid and ethylene glycol, since they form an ethylene glycol solution. The amount of double salts added is from 0.005 to 0.05% (by weight), preferably 0.008 to 0.02%, as the amount of metal versus the dibasic acid.

Additives, such as titanium oxide and carbon black, and copolymer components, such as adipic acid, sodium sulfophthalic acid, and bisphenol A, may be added in this case in addition to the dibasic acid, the ethylene glycol, and the orthoaluminate salt that serves as the catalyst of the present invention. Catalysts such as phosphorous acid, calcium acetate, antimony oxide, and germanium oxide may also be added.

The catalyst of the present invention is used most effectively when producing polyester from the aforementioned dibasic acid and ethylene glycol. Therefore, polyester obtained by using the catalyst of the present invention is an excellent product with good transparency, high softening point, and no fluff or unevenness of drawing.

The present invention is explained in greater detail below through practical and reference examples.

Practical example 1

0.2 part of a double salt of isopropyl aluminate, ethylene glycol, and sodium was added to 100 parts of terephthalic acid and 50 parts of ethylene glycol and heated to 240°C in an autoclave. Reaction was continued for 2 hours while maintaining a pressure of 2.5 kg/cm^2 and removing the water produced. The reaction index was 98%. 0.1 part of triphenyl phosphite and 0.03 part of antimony oxide were added and the mixture was polymerized for 3 hours at 275°C, 0.1 mm Hg. The polymer obtained had an intrinsic viscosity (measured in phenol-tetrachloroethane solvent) of 0.78 and a softening point of 260°C.

Practical example 2

The procedure was exactly the same as in practical example 1 except that 0.25 part of a double salt of isopropyl aluminate, ethylene glycol, and calcium was used instead of the double salt of isopropyl aluminate, ethylene glycol, and sodium. The polymer obtained had an intrinsic viscosity of 0.72 and a softening point of 259°C.

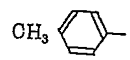
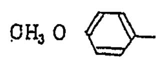
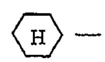
Practical examples 3-6

Table 1 shows the relationships of reaction index and softening point when the type of double salt of aluminic acid ester, ethylene glycol, and alkali metal was varied in the practical examples.

Comparative example 1

Table 1 shows the results obtained when double salt was not added in practical example 1.

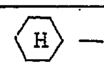
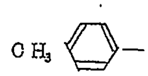
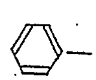
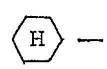
Table 1. Type of catalyst, reaction index, and softening point.

	Type of metal in double salt	Type of R in $Al(OR)_3$ used in double salt preparation	Amount (parts)	Reaction index (%)	Softening point (°C)	[η]
Comparative example 1	-	-	-	92	249	0.72
Practical example 3	Li	CH_3CH_2-	0.15	98	260.5	0.73
Practical example 4	Na		0.25	98	260.0	0.75
Practical example 5	K		0.25	97	260.0	0.72
Practical example 6	K		0.20	97	259.5	0.75

Practical examples 7-11

Table 2 shows the relationships of reaction index and softening point when the double salt of aluminic acid ester, ethylene glycol, and alkaline earth metal was varied in practical example 2.

Table 2

Practical example	Type of metal in double salt	Type of R in $Al(OR)_3$ used in double salt preparation	Amount (parts)	Reaction index (%)	Softening point (°C)	[η]
7	Mg		0.21	97	260.0	0.75
8	Mg		0.25	97	260.0	0.74
9	Ca		0.21	98	259.5	0.75
10	Sr	CH_3CH_2-	0.18	97	259.5	0.78
11	Ba		0.29	98	259.5	0.76

Practical example 12

The procedure was exactly the same as in practical example 1 except that 100 parts of 1,2-bis-p-carboxyphenoxyethane was used instead of terephthalic acid. The reaction index after 3 hours was 99%. The intrinsic viscosity was 0.75 and the softening point was 249°C.

Comparative example 2

No double salt was added in practical example 12. As a result, the reaction index was 95%, the intrinsic viscosity was 0.69, and the softening point was 240°C.

Practical example 15

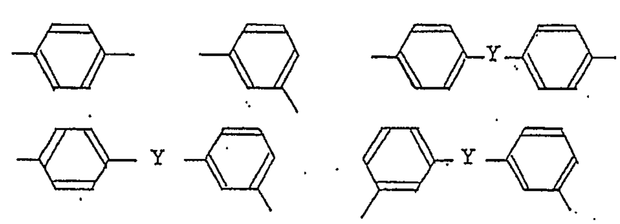
The procedure was exactly the same as in practical example 1 except that the 0.1 part of triphenyl phosphite and 0.03 part of antimony oxide were omitted. The polymer obtained had a intrinsic viscosity of 0.70 and a softening point of 259.5°C. The reaction index after 3 hours was 90% and the softening point was 243°C.

Claim

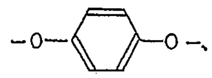
(1) A method for producing polyester polymers involving the reaction of an aromatic dicarboxylic acid represented by the following general formula

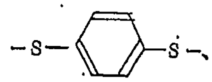
$$HOOCR_1XR_2\text{-}COOH$$

[R_1 and R_2 are $-(CH_2)-$ (n is 0 or an integer of from 1 to 4), X is a bivalent aromatic residue represented by



Y is a bivalent residue represented by $-(CH_2)_n-$, $-(CH_2)_n-CO-(CH_2)_n-$, $-(CH_2)_n-O-(CH_2)_n-$,

$-O-(CH_2)_m-O-$, 

$-(CH_2)_n-S-(CH_2)_n-$, $-S-(CH_2)_n-S-$, 

$-SO_2-$, or $=N-(CH_2)_n-CH_3$, n is 0 or 1-4 and m is 1-5] and ethylene glycol, wherein a double salt obtained by reacting an aluminic acid ester and a compound selected from among alkali metals, alkaline earth metals, and hydrides, alkoxides, glycolates, and phenoxides thereof in ethylene glycol is added.

References

Japanese Kokoku Patents Nos. Sho 31-8596 and Sho 37-9846.

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